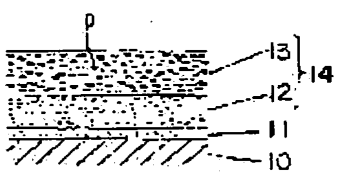
PATENT ABSTRACTS OF JAPAN

(11)Publication number : **06-057396**
(43)Date of publication of application : **01.03.1994**

(51)Int.CI. C23C 4/04
C23C 4/12

(21)Application number : **04-233066**
(22)Date of filing : **07.08.1992**
(71)Applicant : **MAZDA MOTOR CORP**
(72)Inventor : **ASAI YASUSHI**
TAKESHIGE NOBUHIDE
KAWATO YASUSHI
UOSAKI YASUO

(54) FORMATION OF HEAT INSULATING THERMALLY SPRAYED LAYER



(57)Abstract:
PURPOSE: To easily obtain a heat insulating thermally sprayed layer which is uniform, has a high porosity and excellent in the thermal insulation property and, further, to improve the adhesive strength of the boundary between a base layer and the heat insulating thermally sprayed layer and the oxidation resistance, as well.
CONSTITUTION: The base layer 11 is formed on a base material 10 and the thermally sprayed layer 12 of fine ceramic powders excellent in the thermal insulation property is formed thereon and further, powders mixed with the ceramic powders excellent in the thermal insulation property and a specific amount of Si3N4 powders is melt-sprayed to form the thermally sprayed layer 13 having a high porosity. The Si3N4 powders in the mixed powders are heated to a high temperature in the plasma-thermal spraying process and then gasified. Consequently, many porosities remain in the thermally sprayed layer 13 formed in the above-mentioned manner developing the thermally sprayed layer having a high porosity and excellent in the thermal insulation property. On the other hand, since the thermally sprayed layer 12 is dense, it tightly adheres to the base layer 11 and excellent in resistance to oxidation, as well.

CLAIMS

[Claim(s)]
[Claim 1] The formation approach of the thermal-barrier-spraying layer which carries out thermal spraying of ceramic powder and the mixed powder of Si3N4 powder of the specified quantity excellent in adiathermic on a base material, and is characterized by forming a thermal-spraying layer with high porosity.
[Claim 2] The formation approach of the thermal-barrier-spraying layer which forms the precise thermal-spraying layer of the ceramic powder excellent in adiathermic on a base material, carries out thermal spraying of the ceramic powder and the mixed powder of Si3N4 powder of the specified quantity which were excellent in adiathermic on this, and is characterized by forming a thermal-spraying layer with high porosity.
[Claim 3] The formation approach of the thermal-barrier-spraying layer according to claim 1 or 2 characterized by ceramic powder and the mixed powder of Si3N4 powder of the specified quantity excellent in adiathermic being granulation powder.
[Claim 4] The ceramic powder excellent in adiathermic is the formation approach of the thermal-barrier-spraying layer according to claim 1 to 3 characterized by consisting of ZrO 2 andY2O3.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention carries out thermal spraying of the adiathermic outstanding ceramic powder on the surface of a base material, and relates to the formation approach of a thermal-barrier-spraying layer of having been suitable for insulating an engine piston crowning and the interior of an exhaust air system member especially, about the approach of forming a thermal-barrier-spraying layer.
[0002]
[Description of the Prior Art] In order to form a thermal-barrier-spraying layer in a piston crowning in order to raise the temperature of the combustion chamber at the time of engine starting at an early stage, or to prevent the fall of the exhaust gas temperature at the time of engine starting similarly and to raise the purification effectiveness of a catalyst, forming a thermal-barrier-spraying layer in the member inside of an exhaust air system is known conventionally.
[0003] When forming this thermal-barrier-spraying layer, first, the substrate layer for the improvement in adhesion (for example, nickel-Cr layer) is formed in a base material front face, and, subsequently to adiathermic, the plasma metal spray of the powder of excellent ZrO2 grade is carried out. Thus, the formed thermal-spraying layer has pore detailed inside as everyone knows, and the heat insulation property is excellent, so that porosity is high.
[0004] And the porosity of a thermal-spraying layer is adjusted by the grain size of thermal-spraying powder, when detailed powder is used, the thermal-spraying layer in which porosity is inferior to adiathermic comparatively low is formed, and conversely, when the powder of coarse grain is used, the thermal-spraying layer porosity excelled [layer] in adiathermic highly is formed. However, when the powder of coarse grain was used, it was difficult in the thermal-spraying layer to have made homogeneity distribute pore, and it was difficult to obtain the thermal-spraying layer of the high porosity usually exceeding 10% moreover.

[0005] Moreover, detailed powder and the powder of coarse grain are mixed at a fixed rate, a plasma metal spray is carried out on a base material on the conditions on which the powder of coarse grain does not fuse this mixed powder completely, and the method of obtaining the thermal-barrier-spraying layer of high porosity is indicated by JP,63-161150,A. However, selection of the grain size of ceramic powder and a setup of a spray condition are difficult for this approach, and also in order for most powder of coarse grain not to fuse, it has the difficulty that the adhesion of particles tends to become inadequate.
[0006] Furthermore, in the conventional thermal-barrier-spraying layer, when raising heat insulation property and making porosity high utterly, there was also a trouble that the adhesion of a substrate layer-thermal-barrier-spraying layer interface and oxidation-resistant aggravation generally were not avoided.
[0007]
[Problem(s) to be Solved by the Invention] In view of the trouble of the above-mentioned conventional technique, this invention sets it as one purpose to obtain easily the thermal-barrier-spraying layer which was excellent in heat insulation property with uniform and high porosity, and sets it as another purpose further to improve the adhesion of a substrate layer-thermal-barrier-spraying layer interface, and oxidation resistance.
[0008]
[Means for Solving the Problem] Then, it carries out thermal spraying of ceramic powder and the mixed powder of Si_3N_4 powder of the specified quantity excellent in adiathermic on a base material, the formation approach of the thermal-barrier-spraying layer in connection with this invention is characterized by forming a thermal-spraying layer with high porosity, and after forming the precise thermal-spraying layer of the ceramic powder excellent in adiathermic on a base material preferably, it is characterized by forming a thermal-spraying layer with the above-mentioned high porosity. Moreover, in this invention, it is desirable to use ceramic powder and Si_3N_4 powder of the specified quantity excellent in adiathermic as granulation powder, and to carry out thermal spraying of this.
[0009] Although the ceramic which makes ZrO_2 or ZrO_2 a subject, and contains Y_2O_3 as an assistant as a ceramic excellent in adiathermic [which is set as the object of this invention] is suitable, other ceramics used as aluminum2O3 grade and a thermal spray material can be used. In addition, in the approach of this invention, the high thermal-spraying layer or the precise thermal-spraying layer of porosity can also be directly formed on a base material, and can also be formed through substrate layers, such as for example, a nickel-Cr layer.
[0010]
[Function] First, heating at high temperature of this invention is carried out in the thermal-spraying process according [Si_3N_4 powder in mixed powder] to a plasma metal spray etc., and the phenomenon to gasify is used. Since Si_3N_4 powder gasifies, much pores can remain in the thermal-spraying layer formed on the base material, and porosity can form easily the thermal-spraying layer which was highly excellent in adiathermic.
[0011] By the way, in order for pore to obtain the thermal-spraying layer distributed over homogeneity, it is necessary to distribute Si_3N_4 powder over homogeneity in the flow of the mixed powder supplied but, and when the grain size of mixed powder differs greatly, it is difficult in many cases. Moreover, also when the grain size of the powder supplied is small to remainder, it may be difficult to obtain the thermal-spraying layer from which powdered flow is not stabilized but pore is distributed over

homogeneity. Then, in this invention, in order to acquire more uniform pore distribution, mixed powder was used as granulation powder, and it carried out to making homogeneity distribute Si3N4 powder in granulation powder. In this case, when there is no limit especially in the grain size of the ceramic powder excellent in adiathermic, and Si3N4 powder, for example, Si3N4 detailed powder is used, detailed pore can obtain the thermal-spraying layer distributed over homogeneity.
[0012] In this invention, the porosity of a thermal-spraying layer is adjusted with the addition of Si3N4 powder in mixed powder, and the desirable addition range is 5 - 15 % of the weight. That is, if there is not effectiveness sufficient at less than 5% for pore formation and 15% is exceeded, while pore will make it big and rough, it is to continuation-become easy toize and for the adhesion of an interface with a substrate layer or a precise thermal-spraying layer to get worse.
[0013] By above-mentioned being within the limits and adding Si3N4 powder, the porosity of a thermal-spraying layer can be made into about 10 - 25%, and a thermal-spraying layer with high porosity with high heat insulation property can be obtained. In addition, even if the porosity of the thermal-spraying layer when not adding Si3N4 powder is high, it is only about 5 - 10%. Although the graph of 8%Y2O3-92% ZrO2 of thermal conductivity and porosity is shown in drawing 2 as one example, in the porosity range obtained by this invention, thermal conductivity is still smaller and it turns out that adiathermic is excellent.
[0014] furthermore, the time of forming a thermal-spraying layer with the above-mentioned high porosity, after forming the precise thermal-spraying layer of the ceramic powder excellent in adiathermic on a base material in this invention -- this -- since a precise thermal-spraying layer is excellent in the adhesion of a base material (or substrate layer) and an interface and excellent also in oxidation resistance, it can obtain the thermal-barrier-spraying layer which has the special feature which was excellent in both as a whole.
[0015]
[Example] Hereafter, one at the time of forming a thermal-barrier-spraying layer on a base material using the approach of this invention of a production process is explained with reference to the block diagram shown in drawing 3 . (1) First, using cast iron (FCD500) as a base material, use solvents, such as (2) acetones, and it is shot blasting about washing, cleaning, and (3) base-material front face. Abrasive is the alumina particle of 40-50 meshes of grain size, and is 4kg/cm2 of blasting **. (4) Form the substrate layer of 30-micrometer thickness on a base material by the plasma metal spray. A thermal spray material is 80nickel-20Cr alloy powder with a particle size of 10-45 micrometers. (5) Form the precise thermal-spraying layer of 200-micrometer thickness on a substrate layer by the plasma metal spray. A thermal spray material is 8%Y2O3-92%ZrO2 powder with a particle size of 5-35 micrometers. (6) Form a thermal-spraying layer with the high porosity of 300-micrometer thickness by the plasma metal spray. A thermal spray material is granulation powder (refer to drawing 4) with a particle size of 10-45 micrometers which blended Si3N4 powder with a particle size of 2 micrometers or less 10%, and carried out mixing granulation to 8%Y2O3-92%ZrO2 powder with a particle size of 5 micrometers or less.
[0016] The cross section of the thermal-barrier-spraying layer formed of the above-mentioned process is shown in drawing 1 . According to drawing 1 , the substrate layer 11 is formed on a base material 10, and the thermal-spraying layer 13 with high porosity is formed on it on it at the precise thermal-spraying layer 12 and the pan. It is the pore which p shows. As shown here, the porosity of the thermal-spraying layer 12 is small, and since Si3N4 gasified and dispersed, the porosity of the thermal-spraying

layer 13 is high. Since the thermal-barrier-spraying layer 14 in this example consists of two-layer [of the precise thermal-spraying layer 12 and the thermal-spraying layer 13 with high porosity], while its adiabatic efficiency is high, its adhesion with the substrate layer 2 is good, and it has the property that oxidation resistance is also high.
[0017] With reference to block drawing 3 with one same process, it explains conventionally for a comparison. A different point from the above-mentioned example is a point which formed about 500-micrometer thermal-spraying layer on the substrate layer by (7) plasma metal sprays instead of the above (5) and the process of (6). The grain size of 8%Y2O3-92%ZrO2 used powder is also large with 45-100 micrometers. The cross section of the thermal-barrier-spraying layer formed of the process conventionally [this] is shown in drawing 5 R> 5. Although the thermal-barrier-spraying layer 15 is formed on the substrate layer 11, since the porosity is not enough compared with the thermal-spraying layer 13 of the above-mentioned example, it is inferior to adiathermic, and since porosity is conversely large compared with the thermal-spraying layer 12 of the above-mentioned example, it is inferior to adhesion with the substrate layer 11, and oxidation resistance.
[0018]
[Effect of the Invention] When according to this invention the thermal-spraying layer of high porosity is formed after being able to obtain easily the thermal-barrier-spraying layer which was excellent in heat insulation property with uniform and high porosity and forming the still more precise thermal-spraying layer on the base, the thermal-barrier-spraying layer improved also about adhesion with a base or a substrate layer and oxidation resistance can be obtained.

TECHNICAL FIELD

[Industrial Application] This invention carries out thermal spraying of the adiathermic outstanding ceramic powder on the surface of a base material, and relates to the formation approach of a thermal-barrier-spraying layer of having been suitable for insulating an engine piston crowning and the interior of an exhaust air system member especially, about the approach of forming a thermal-barrier-spraying layer.

PRIOR ART

[Description of the Prior Art] In order to form a thermal-barrier-spraying layer in a piston crowning in order to raise the temperature of the combustion chamber at the time of engine starting at an early stage, or to prevent the fall of the exhaust gas temperature at the time of engine starting similarly and to raise the purification effectiveness of a catalyst, forming a thermal-barrier-spraying layer in the member inside of an exhaust air system is known conventionally.
[0003] When forming this thermal-barrier-spraying layer, first, the substrate layer for the improvement in adhesion (for example, nickel-Cr layer) is formed in a base material front face, and, subsequently to adiathermic, the plasma metal spray of the powder of excellent ZrO2 grade is carried out. Thus, the formed thermal-spraying layer has pore detailed inside as everyone knows, and the heat insulation property is excellent, so that porosity is high.
[0004] And the porosity of a thermal-spraying layer is adjusted by the grain size of thermal-spraying powder, when detailed powder is used, the thermal-spraying layer in

which porosity is inferior to adiathermic comparatively low is formed, and conversely, when the powder of coarse grain is used, the thermal-spraying layer porosity excelled [layer] in adiathermic highly is formed. However, when the powder of coarse grain was used, it was difficult in the thermal-spraying layer to have made homogeneity distribute pore, and it was difficult to obtain the thermal-spraying layer of the high porosity usually exceeding 10% moreover.

[0005] Moreover, detailed powder and the powder of coarse grain are mixed at a fixed rate, a plasma metal spray is carried out on a base material on the conditions on which the powder of coarse grain does not fuse this mixed powder completely, and the method of obtaining the thermal-barrier-spraying layer of high porosity is indicated by JP,63-161150,A. However, selection of the grain size of ceramic powder and a setup of a spray condition are difficult for this approach, and also in order for most powder of coarse grain not to fuse, it has the difficulty that the adhesion of particles tends to become inadequate.

[0006] Furthermore, in the conventional thermal-barrier-spraying layer, when raising heat insulation property and making porosity high utterly, there was also a trouble that the adhesion of a substrate layer-thermal-barrier-spraying layer interface and oxidation-resistant aggravation generally were not avoided.

EFFECT OF THE INVENTION

[Effect of the Invention] When according to this invention the thermal-spraying layer of high porosity is formed after being able to obtain easily the thermal-barrier-spraying layer which was excellent in heat insulation property with uniform and high porosity and forming the still more precise thermal-spraying layer on the base, the thermal-barrier-spraying layer improved also about adhesion with a base or a substrate layer and oxidation resistance can be obtained.

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] In view of the trouble of the above-mentioned conventional technique, this invention sets it as one purpose to obtain easily the thermal-barrier-spraying layer which was excellent in heat insulation property with uniform and high porosity, and sets it as another purpose further to improve the adhesion of a substrate layer-thermal-barrier-spraying layer interface, and oxidation resistance.

MEANS

[Means for Solving the Problem] Then, it carries out thermal spraying of ceramic powder and the mixed powder of Si_3N_4 powder of the specified quantity excellent in adiathermic on a base material, the formation approach of the thermal-barrier-spraying layer in connection with this invention is characterized by forming a thermal-spraying layer with high porosity, and after forming the precise thermal-spraying layer of the ceramic powder excellent in adiathermic on a base material preferably, it is characterized by forming a thermal-spraying layer with the above-mentioned high porosity. Moreover, in this invention, it is desirable to use ceramic

powder and Si_3N_4 powder of the specified quantity excellent in adiathermic as granulation powder, and to carry out thermal spraying of this.
[0009] Although the ceramic which makes ZrO_2 or ZrO_2 a subject, and contains Y_2O_3 as an assistant as a ceramic excellent in adiathermic [which is set as the object of this invention] is suitable, other ceramics used as aluminum2O3 grade and a thermal spray material can be used. In addition, in the approach of this invention, the high thermal-spraying layer or the precise thermal-spraying layer of porosity can also be directly formed on a base material, and can also be formed through substrate layers, such as for example, a nickel-Cr layer.

OPERATION

[Function] First, heating at high temperature of this invention is carried out in the thermal-spraying process according [Si_3N_4 powder in mixed powder] to a plasma metal spray etc., and the phenomenon to gasify is used. Since Si_3N_4 powder gasifies, much pores can remain in the thermal-spraying layer formed on the base material, and porosity can form easily the thermal-spraying layer which was highly excellent in adiathermic.
[0011] By the way, in order for pore to obtain the thermal-spraying layer distributed over homogeneity, it is necessary to distribute Si_3N_4 powder over homogeneity in the flow of the mixed powder supplied but, and when the grain size of mixed powder differs greatly, it is difficult in many cases. Moreover, also when the grain size of the powder supplied is small to remainder, it may be difficult to obtain the thermal-spraying layer from which powdered flow is not stabilized but pore is distributed over homogeneity. Then, in this invention, in order to acquire more uniform pore distribution, mixed powder was used as granulation powder, and it carried out to making homogeneity distribute Si_3N_4 powder in granulation powder. In this case, when there is no limit especially in the grain size of the ceramic powder excellent in adiathermic, and Si_3N_4 powder, for example, Si_3N_4 detailed powder is used, detailed pore can obtain the thermal-spraying layer distributed over homogeneity.
[0012] In this invention, the porosity of a thermal-spraying layer is adjusted with the addition of Si_3N_4 powder in mixed powder, and the desirable addition range is 5 - 15 % of the weight. That is, if there is not effectiveness sufficient at less than 5% for pore formation and 15% is exceeded, while pore will make it big and rough, it is to continuation-become easy toize and for the adhesion of an interface with a substrate layer or a precise thermal-spraying layer to get worse.
[0013] By above-mentioned being within the limits and adding Si_3N_4 powder, the porosity of a thermal-spraying layer can be made into about 10 - 25%, and a thermal-spraying layer with high porosity with high heat insulation property can be obtained. In addition, even if the porosity of the thermal-spraying layer when not adding Si_3N_4 powder is high, it is only about 5 - 10%. Although the graph of 8%Y_2O_3-92% ZrO_2 of thermal conductivity and porosity is shown in <u>drawing 2</u> as one example, in the porosity range obtained by this invention, thermal conductivity is still smaller and it turns out that adiathermic is excellent.
[0014] furthermore, the time of forming a thermal-spraying layer with the above-mentioned high porosity, after forming the precise thermal-spraying layer of the ceramic powder excellent in adiathermic on a base material in this invention -- this -- since a precise thermal-spraying layer is excellent in the adhesion of a base material (or substrate layer) and an interface and excellent also in oxidation resistance, it can

obtain the thermal-barrier-spraying layer which has the special feature which was excellent in both as a whole.

EXAMPLE

[Example] Hereafter, one at the time of forming a thermal-barrier-spraying layer on a base material using the approach of this invention of a production process is explained with reference to the block diagram shown in drawing 3 . (1) First, using cast iron (FCD500) as a base material, use solvents, such as (2) acetones, and it is shot blasting about washing, cleaning, and (3) base-material front face. Abrasive is the alumina particle of 40-50 meshes of grain size, and is 4kg/cm2 of blasting **. (4) Form the substrate layer of 30-micrometer thickness on a base material by the plasma metal spray. A thermal spray material is 80nickel-20Cr alloy powder with a particle size of 10-45 micrometers. (5) Form the precise thermal-spraying layer of 200-micrometer thickness on a substrate layer by the plasma metal spray. A thermal spray material is 8%Y2O3-92%ZrO2 powder with a particle size of 5-35 micrometers. (6) Form a thermal-spraying layer with the high porosity of 300-micrometer thickness by the plasma metal spray. A thermal spray material is granulation powder (refer to drawing 4) with a particle size of 10-45 micrometers which blended Si3N4 powder with a particle size of 2 micrometers or less 10%, and carried out mixing granulation to 8%Y2O3-92%ZrO2 powder with a particle size of 5 micrometers or less.
[0016] The cross section of the thermal-barrier-spraying layer formed of the above-mentioned process is shown in drawing 1 . According to drawing 1 , the substrate layer 11 is formed on a base material 10, and the thermal-spraying layer 13 with high porosity is formed on it on it at the precise thermal-spraying layer 12 and the pan. It is the pore which p shows. As shown here, the porosity of the thermal-spraying layer 12 is small, and since Si3N4 gasified and dispersed, the porosity of the thermal-spraying layer 13 is high. Since the thermal-barrier-spraying layer 14 in this example consists of two-layer [of the precise thermal-spraying layer 12 and the thermal-spraying layer 13 with high porosity], while its adiabatic efficiency is high, its adhesion with the substrate layer 2 is good, and it has the property that oxidation resistance is also high.
[0017] With reference to block drawing 3 with one same process, it explains conventionally for a comparison. A different point from the above-mentioned example is a point which formed about 500-micrometer thermal-spraying layer on the substrate layer by (7) plasma metal sprays instead of the above (5) and the process of (6). The grain size of 8%Y2O3-92%ZrO2 used powder is also large with 45-100 micrometers. The cross section of the thermal-barrier-spraying layer formed of the process conventionally [this] is shown in drawing 5 R> 5. Although the thermal-barrier-spraying layer 15 is formed on the substrate layer 11, since the porosity is not enough compared with the thermal-spraying layer 13 of the above-mentioned example, it is inferior to adiathermic, and since porosity is conversely large compared with the thermal-spraying layer 12 of the above-mentioned example, it is inferior to adhesion with the substrate layer 11, and oxidation resistance.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is the cross section of the thermal-barrier-spraying layer formed of the

process of an example.
[Drawing 2] It is drawing showing the relation of 8%Y2O3-92% ZrO2 of thermal conductivity and porosity.
[Drawing 3] It is the block diagram showing the process which forms a thermal-barrier-spraying layer on a base material.
[Drawing 4] It is the mimetic diagram of the granulation powder which consists of Y2O3-92%ZrO2 powder and Si3N4 powder.
[Drawing 5] It is the cross section of the thermal-barrier-spraying layer formed of the process of the conventional example.
[Description of Notations]
10 Base Material
11 Substrate Layer
12 Precise Thermal-Spraying Layer
13 Thermal-Spraying Layer with High Porosity
14 Thermal-Barrier-Spraying Layer of this Invention
15 The Conventional Thermal-Barrier-Spraying Layer